μg) similar procedures indicated *ca.* 1%[10] conversion to material behaving like cholesterol [or 25,26,27-trisnorcholesterol (XV)] on tlc. Cocrystallization of a portion of this material (4536 dpm) with authentic XV, 23.7 mg (mp 132–133.5°, synthesized by standard methods from 3β-hydroxy-Δ^5-cholenic acid, correct infrared, nmr, and elemental analysis), gave a loss of 30% of the activity. Acetylation and further recrystallization gave no further loss of activity, but purification (as for cholesterol) *via* the dibromide resulted in retention of only 10% of the original radioactivity.

The results suggest that both 2,3-dihydrosqualene and 1,1′,2-trisnorsqualene can act as substrates for the squalene oxidase that normally converts squalene to the 2,3-oxide, and that trisnorlanosterol may be converted to other sterols of the trisnorcholestane series (but with poor efficiency) by the enzymes that normally oxidize lanosterol to cholesterol. Conversion of dihydrolanosterol and other 24,25-dihydrosterols to cholesterol is already well established.[11]

Acknowledgment. This research was supported by National Institutes of Health Grants AI 05102 and GM 10421 (to E. E. v. T.) and GM 12493 (to R. B. C.), and a Grant-in-Aid from the American Heart Association (to R. B. C.). The authors are grateful to Miss K. E. Lord for invaluable assistance in carrying out the incubations, and to Dr. A. Duffield for mass spectral determinations on substances produced by nonenzymic means.

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[10] It should be noted that the present studies do not permit conclusions concerning the relative efficiencies of utilization of the oxides IV and VI, or of the hydrocarbons III and V, since different concentrations of substrates and different liver enzyme preparations were used in the various experiments. Further work directed toward a quantitative comparison of these substrates is in progress.

[11] R. B. Clayton, *Quart. Rev.* (London), **19**, 168 (1965).

[12] National Institutes of Health Predoctoral Fellow.

[13] National Institutes of Health Postdoctoral Fellow.

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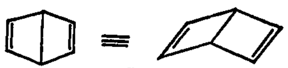
Nonaromatization Reactions of Bicyclo[2.2.0]hexa-2,5-diene

Sir:

Despite the passage of some years since the first bicyclo[2.2.0]hexa-2,5-dienes (nonplanar "Dewar benzenes") (I) were reported,[1] the subsequent identification of additional cases in other laboratories,[2a,b] and the commercial availability of one of these,[3] very little is known about the chemical behavior of this high-energy strained system. We have studied the interaction of parent "Dewar benzene" with various electrophilic species, finding that the reactions usually do not involve aromatization but characteristically provide nonbenzenoid transformation products.

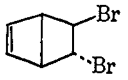


I

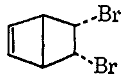
Oxidation of bicyclo[2.2.0]hexa-2,5-diene[4] with 0.46 *M* *m*-chloroperbenzoic acid in diethyl ether at room temperature afforded the 2,3-oxide II, a colorless oil at room temperature (75% yield). The nmr spectrum of the oxide exhibited signals at τ 3.61 (H-5, -6; broad singlet), 5.97 (H-2, -3; doublet) and 6.68 (H-1, -4; broad singlet), all in the integrated ratio 1:1:1. In a mass spectral determination, the molecular ion (*m/e* 94) appeared as a major peak, accompanied by more intense peaks at *m/e* 78 and 44. After being heated neat at 115° ($t_{1/2} \cong$ 16 min) or being irradiated with a low-pressure mercury lamp at room temperature in *n*-pentane solution for *ca.* 1 hr, epoxide II isomerized to oxepin–benzene oxide (III), which was identified (vpc, nmr, ultraviolet) by comparison with authentic material.[5] Although no phenol was detected after epoxidation of I, it was produced during the thermolysis and photolysis reactions of II.

II III

On being treated with 0.5 mmole of bromine in alkane solution at 0° for 10 min, "Dewar benzene" (*ca.* 1 mmole) was converted in 97% yield to an oily mixture of dibromides (IV).[6] No bromobenzene was detected. After rapid chromatography of IV, a pure component, the 2,3-*trans*-dibromide IVa, could be isolated [nmr spectrum: τ 3.52 (broad singlet), 3.67 (broad singlet), 5.32 (multiplet), 5.80 (doublet; J = 4 cps), 6.25 (multiplet); integrated ratio 1:1:1:1:2, respectively]. Ozonolysis of IVa, including an oxidative work-up with peracetic acid, provided 3,4-*trans*-dibromocyclobutane-*cis*-1,2-dicarboxylic acid (V), which as the diester was found to be identical (infrared, nmr) with an authentic specimen.[7] Catalytic hydrogenolysis [5% Pd–C, Et_3N (fourfold excess)] of V dimethyl ester led to dimethyl cyclobutane-*cis*-1,2-dicarboxylate ester (VI), direct comparison with the known substance being carried out.[8]



IVa



IVb

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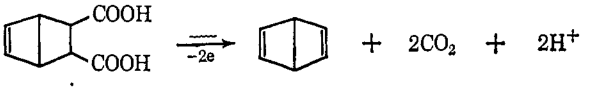
[1] (a) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962); (b) E. E. van Tamelen and S. P. Pappas, *ibid.*, **85**, 3297 (1963).

[2] For a partial list, see: (a) E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 738 (1965); (b) H. G. Viehe, *Angew. Chem.*, **77**, 768 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 746 (1965).

[3] W. Schäfer, *Angew. Chem.*, **78**, 716 (1966).

[4] The hydrocarbon used herein was prepared by the electrolytic decarboxylation of acid i, a reaction first performed by Mr. T. Whitesides (unpublished results secured in this laboratory).



i

[5] E. Vogel, W. A. Boll, and H. Günther, *Tetrahedron Letters*, 609 (1965).

[6] With larger proportions of bromine, "Dewar benzene" is converted to a crystalline tetrabromide, mp 120–120.5°.

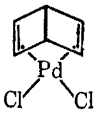
[7] E. Vogel, *Ann.*, **615**, 14 (1958).

[8] N. L. Allinger, *J. Org. Chem.*, 30, 1945 (1965).

Although the second dibromide was too unstable to permit purification, the nmr spectrum of the original mixture clearly revealed the presence of this component [τ 2.97 (triplet; $J = 2$ cps), 5.60 (singlet), 6.82 (triplet; $J = 2$ cps); integrated ratio 1:1:1], apparently the *cis*-dibromide IVb (*cis*:*trans* ratio 30:70, by nmr). This assignment was supported by the results of an ozonization–hydrogenolysis sequence, as above, but carried out on the dibromide mixture; dicarboxylate ester VI was found in an amount (61%) not greatly different from that secured (67%) from the pure *trans* case.[9] Furthermore, the mass spectra (molecular ion m/e 238) of IVa and the *cis–trans* mixture were essentially identical.

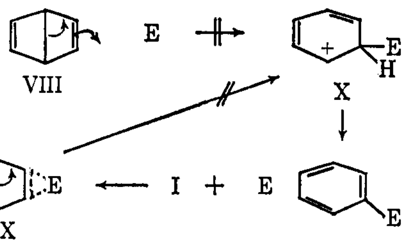
Excess osmium tetroxide in ether at room temperature converted "Dewar benzene" to a tetrol, mp 184–186°; nmr data: broad singlets at τ 5.25, 5.97, 7.72, all in the integrated ratio of 2:2:1; the low-field signal at τ 5.25 disappears under deuterium-exchange conditions; strongly periodate positive. The oxidation product revealed the following mass spectral behavior: molecular ion m/e 146 (weak), 128, 110, 99, 86, 73 (base peak), 60, 57, 55, 53, 45. In the reaction system, osmium tetroxide neither detectably isomerized I to benzene nor converted it to phenol.

A relatively stable metal coordination complex (VII) of "Dewar benzene" was prepared by interaction of the hydrocarbon with bis(benzonitrile)palladium dichloride in methylene dichloride.[10] Precipitating from the reaction solution, the light brown amorphous solid exhibited infrared behavior (7.18, 7.97, 8.51, 10.05 μ) consonant with the assigned structure. As in the norbornadiene–rhodium(I) acetylacetonate case,[11] the olefinic protons are shifted in the nmr spectrum to the higher field position of the methine hydrogens (τ 5.60 (broad singlet)). While the reaction mixture was being observed by nmr means, the displacement of hydrocarbon ligand by pyridine-d_5 was carried out; bicyclohexadiene was released, but no detectable amount of Kekulé benzene was generated. The above data preclude the structural possibility benzene–palladium dichloride, which in fact remains unknown.



VII

On the basis of the above examples, an olefinic bond in "Dewar benzene" is prone to interact with an electron-deficient species while retaining a cyclobutene unit, despite the availability of an aromatization pathway (VIII or IX → X) involving an isomerization of the well-recognized cyclobutyl → homoallyl cation type.



It thus appears that the orbital symmetry factors which inhibit nonphotochemical conversion of "Dewar benzene" to Kekule benzene[2a] can operate as well in the transition state of a reaction with an external agent.

Acknowledgment. The authors are grateful to the Army Research Office (Durham) (Grant 5227-C) for financial support and to Professor N. Allinger, Wayne State University, for kindly providing samples of cyclobutane-1,2- and -1,3-dicarboxylic esters.

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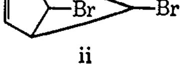
[9] There was detected also a 0.7% yield of acid which was indistinguishable (by vpc on the diester) from cyclobutane-*cis*-1,3-dicarboxylic acid.[8] This tentatively identified substance may find its origin in



ii

small amounts of the abnormal bromination product ii.

[10] A close precedent is the formation of an olefin complex from palladium dichloride and norbornadiene: R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82,** 535 (1960).

[11] Observation made in this laboratory.

Photolytic Production of Hydrated Electrons from Aqueous Potassium Octacyanomolybdate(IV) and Potassium Octacyanotungstate(IV)

Sir:

We wish to report some observations on the flash photolysis of aqueous potassium octacyanomolybdate(IV), $K_4[Mo(CN)_8]\cdot 2H_2O$, and potassium octacyanotungstate(IV), $K_4[W(CN)_8]\cdot 2H_2O$. The investigation was prompted by recent observations[1–4] that photoelectron production occurs with aqueous ferrocyanide ion plus some considerations as to what desirable properties one should look for in searching for other complex cyanides that might behave similarly. The prerequisites assumed were that (a) the wavelength region illuminated by a conventional flash system should contain absorption bands of a charge-transfer character, (b) there be a reasonably stable complex of the same stoichiometry and one higher oxidation state, and (c) that there be no stable complex of the same stoichiometry and one lower oxidation state (so that electron scavenging would not be important). The above octacyanides meet these criteria admirably; both show fairly intense adsorption features in the near ultraviolet,[5] the oxidation potentials to the corresponding V valence state compounds are 0.84 and 0.57 v for $Mo(CN)_8^{-4}$ and $W(CN)_8^{-4}$, respectively,[6] and no III valence-state octacyanides are known. Only the complex $K_4[Mo(CN)_7]\cdot 2H_2O$ has been reported,[7] and it is dubious whether the molybdenum(III) octacyanide

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[1] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, **67,** 2613 (1963).

[2] G. Stein, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, pp 238–240.

[3] P. L. Airey and F. S. Dainton, *Proc. Roy. Soc.* (London), **A291,** 340 (1966).

[4] S. Ohne and G. Tsuchihashi, *Bull. Chem. Soc. Japan,* **38,** 1052 (1965).

[5] A. W. Adamson and J. R. Perumarreddi, *Inorg. Chem.*, **4,** 247 (1965).

[6] B. N. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8,** 83 (1966).

[7] R. C. Young, *J. Am. Chem. Soc.*, **54,** 1402 (1932).